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BRIEF COMMUNICATIONS

QUANTUM CHEMICAL MODELING OF THE STRUCTURE OF STRAINED SILICON NANOCRYSTALS

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The results of the atomic structure optimization and the calculation of electronic characteristics for strained silicon clusters Si_{51} on a germanium substrate are presented. The effects of deformation and the substrate on the distribution of electron state are analyzed.

Keywords: nanocrystal, nanostructure, cluster, silicon, electronic properties, deformation, substrate.

Currently the construction of semiconductor devices is turning to the level of nanotechnologies, and owing to this, clusters of different semiconductors as potential eliminators for bulk crystalline materials become the objects of intensive researches [1-4]. These researches are necessary to predict the properties of semiconductor products because for the same number of atoms in nanostructures their bond energy, electron density distribution, energy spectrum, and other significant parameters change when their geometry relatively slightly varies.

Of great interest are now the investigations of properties of silicon nanostructures obtained on the substrates with lattice parameters different from those of crystalline silicon, and hence, in the strained state [5-7]. According to the literature data, in the theoretical analysis of silicon nanostructures on substrates only the crystal lattice rupture in one or two directions is taken into account [8, 9], but not the finite number of atoms and the substrate presence. The use of some general model representations of quantum objects does not always give an explanation to arising effects and peculiarities of one or another structure. Therefore it is essential to more thoroughly consider the properties of silicon nanostructures on substrates.

In the present work, some electronic properties of strained silicon nanoparticles on a germanium substrate are computed with taking into account the interaction effects of the cluster atoms adjoining the substrate.

Calculation procedure. In practice the force mechanics and molecular dynamics methods are used, as a rule, to calculate the optimal geometry of molecules. Currently, one of the most approved experimentally methods is MM+, the modification of the MM2 force field [10]. The main improvement of MM+ in comparison with MM2 is that the deformation energy is considered with accuracy up to third order of magnitude, and the deformation energy of valence angles is computed up to sixth order of magnitude. For the diatomic molecule of Si_2 the MM+ calculation produces the bond length of 0.222 nm at its experimental value of 0.225 nm [11] (deviation 1.3%), whereas a semiempirical MP3 calculation gives the bond length of 0.229 nm (deviation from experimental 1.8%). This example clearly demonstrates that the MM+ application to determine the geometry of silicon structures provide the error comparable with a rather precise quantum chemical method.

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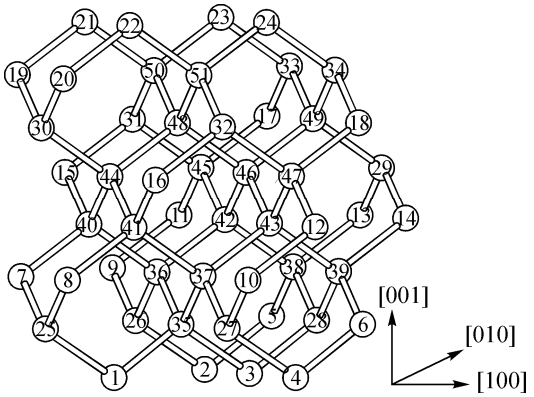

Fig. 1. Geometry of undistorted Si_{51} nanostructure.

To study the electronic properties of silicon clusters we applied the semiempirical quantum chemical method of partial neglecting the diatomic differential overlapping NDDO PM3 [3, 12]. This calculation method was chosen because at present PM3 is one of most precise, optimized on a large experimental material. The results of PM3 application to compute the electronic characteristics of silicon clusters, as shown in the works [1,3], correspond to the experimental data much better than the results of the *ab initio* calculation in the 6-31G basis set. The atomic charge was determined by the Mulliken method [3, 13].

Results and Discussion. To take into account the effects of deformation and interaction with a substrate on the structure properties four types of silicon nanocrystals were considered.

Structure **1** is a silicon nanocrystal as an ideal lattice cluster of undistorted silicon (with a lattice constant of 5.431 Å). As an object of investigation the structure consisting of eight crystal unit cells (2×2×2) was taken, the atoms with only one bond being removed. Finally, we obtained the structure with 51 atoms Si_{51} shown in Fig. 1. In this figure the surface atoms with two vacant bonds have the order numbers from 1 to 24, the intermediates with three bonds 25-34, and internal with four bonds 35-51.

Structure **2** is a silicon nanocrystal Si_{51} as a cluster of single-crystal silicon stretched along the (001) plane and contracted in the [001] direction. The value of stretching in [100] and [010] directions was taken as 4% (the difference between the lattice constants of silicon and germanium), the value of contraction in the [001] direction, according to [7, 14], was determined as 3.1%.

Structure **3** is the starting silicon structure of type 2 optimized by MM+, the coordinates of the lower atoms (*1-4* in Fig. 1) being fixed to model the adherence to the substrate.

Structure **4** is the starting structure of type 2 with the interaction effects between the interfacial atoms (atoms *1-4* in the Fig. 1) of the silicon cluster and the germanium substrate considered by saturating with hydrogen the unsaturated bonds of these atoms. Then the geometry of the structure was optimized by MM+, the position of silicon interfacial atoms saturated with hydrogen being fixed. The saturation of vacant bonds of silicon atoms adjoining the substrate with hydrogen is explained by similar electronegativity values for hydrogen and germanium [11]. Note that visual differences between structures **2**-**4** and structure **1** are almost inconspicuous in the Fig. 1 scale.

For above structures **1**-**4** the coordinates and effective atomic charges are determined which give an opportunity for discussing the degree of occupation of orbitals and the electrostatic potential distribution inside the nanocrystal and near its surface.

For structures **1** and **2,** the average bond lengths were determined according to [7, 14] from the values of lattice constants of single crystal silicon with taking into account lattice deformations and were 2.352 Å and 2.391 Å respectively. As the analysis of MM+ optimized structure **3** shown**,** the bond lengths of neighboring silicon atoms in this structure without taking into account the interactions between cluster atoms and the substrate fall within a range from 2.329 Å to 2.376 Å (the

TABLE 1. Effective Atomic Charges in the Nanostructures (in elementary charge units *e*)

No. of atom	Structure				No. of atom	Structure			
	1	**2**	**3**	**4**		**1**	**2**	**3**	**4**
1	0.315	0.249	0.258	0.173	27	–0.053	–0.091	–0.086	–0.015
2	0.118	0.111	0.127	0.076	28	–0.171	–0.228	–0.236	–0.139
3	0.293	0.299	0.333	0.067	29	–0.143	–0.164	–0.159	–0.01
4	0.115	0.112	0.127	0.064	30	–0.090	–0.104	–0.055	–0.041
5	0.191	0.198	0.191	0.377	31	–0.232	–0.170	–0.163	–0.171
6	0.184	0.198	0.191	0.373	32	–0.169	–0.171	–0.163	–0.171
7	0.252	0.329	0.312	0.303	33	–0.165	–0.119	–0.151	–0.143
8	0.314	0.329	0.312	0.298	34	–0.143	–0.118	–0.151	–0.140
9	0.127	0.138	0.108	0.154	35	–0.270	–0.263	–0.251	–0.118
10	0.114	0.138	0.108	0.157	36	–0.201	–0.192	–0.201	–0.188
11	0.195	0.215	0.19	0.215	37	–0.297	–0.192	–0.201	–0.185
12	0.184	0.215	0.19	0.215	38	–0.239	–0.215	–0.221	–0.248
13	0.278	0.286	0.297	0.236	39	–0.259	–0.214	–0.221	–0.248
14	0.255	0.286	0.297	0.233	40	–0.266	–0.271	–0.270	–0.248
15	0.333	0.267	0.287	0.284	41	–0.270	–0.271	–0.270	–0.244
16	0.293	0.268	0.287	0.288	42	–0.227	–0.207	–0.216	–0.195
17	0.300	0.295	0.271	0.268	43	–0.224	–0.207	–0.216	–0.193
18	0.253	0.294	0.271	0.264	44	–0.205	–0.28	–0.299	–0.297
19	0.127	0.122	0.105	0.101	45	–0.222	–0.257	–0.239	–0.224
20	0.117	0.122	0.105	0.102	46	–0.255	–0.231	–0.251	–0.271
21	0.194	0.172	0.189	0.18	47	–0.261	–0.256	–0.239	–0.22
22	0.189	0.172	0.189	0.179	48	–0.224	–0.225	–0.219	–0.204
23	0.295	0.221	0.252	0.237	49	–0.082	–0.110	–0.070	–0.138
24	0.275	0.222	0.252	0.238	50	–0.218	–0.257	–0.264	–0.251
25	–0.094	–0.095	–0.092	–0.07	51	–0.238	–0.257	–0.264	–0.252
26	–0.092	–0.091	–0.086	–0.016					

mean is 2.349 Å); with taking into account the interactions with the substrate (structure **4**), the bond lengths are from 2.309 Å to 2.384 Å, the mean slightly lessening to 2.348 Å. For both structures the largest values of bond lengths are typical of the internal spheres of the nanoclusters. Thus, in transition from structure **1** to structure **2** the average bond length naturally increases due to stretching deformation, however, the succeeding optimization of the structure restores the average bond length to a value close to that of crystalline silicon (structures **3**, **4**).

Table 1 lists the computed effective charges for all the atoms in nanostructures **1**-**4**. As it follows from this table, the charge distribution and the electron occupation of atoms at a large extent depend on the geometry of the structure, which corresponds to the results of the works [1-4]. The mean charge value varies most substantially in passing to structure **4**, while for structures **1**-**3** the mean charge values change less significantly. For all the structures in question the mean charge of atoms on the surface is positive (~ +0.2*e*) and negative (~ –0.2*e*) for internal ones. Hence, the potential on the surface is also positive relative to the internal part of the structure, and the concentration of free charge carriers is higher on the surface than in the bulk, which corresponds to experimental data from the study of surface properties of bulk silicon crystals [14]. Here the charge is positive only for the atoms with two vacant bonds. Note that for structures **1**-**3** in which the interaction with the substrate is not taken into account and which actually represent an isolated cluster in a vacuum the interfacial silicon atoms (*1*-*4*) do not differ by the charge value from other surface atoms. The mean effective charges on these atoms are +0.210 *e*, +0.193 *e*, and +0.211*e* for structures **1**, **2,** and **3** respectively. However, if we take into account the interactions between the

TABLE 2. Some Energy Characteristics of the Nanostructures under Study, eV

Characteristic	Structure			
	1	**2**	**3**	**4**
Bond energy	–193.54	–192.37	–193.44	–218.70
Upper occupied state	–7.16	–7.15	–7.18	–7.05
Lower unoccupied state	–4.86	–4.75	–4.91	–4.73
HOMO–LUMO gap	2.30	2.40	2.27	2.32
Point symmetry group	C_{3v}	C_s	C_s	C_1

interfacial atoms and the germanium substrate (saturated with hydrogen) in structure **4,** it results in a considerable decrease of the mean charge value on these atoms — up to a value of +0.095*e*. Nevertheless, these atoms still preserve the positive sign of the charge and, correspondingly, the positive potential, which is qualitatively correct because the electronegativity of germanium (2.0) is somewhat higher than that of silicon (1.9) [11]. Moreover, as it follows from experiment, on the interface of bulk Ge and Si crystals a positive charge appears in silicon [14].

Based on our PM3 calculation of the energy parameters listed in Table 2, it is possible to make a conclusion that when a silicon nanocluster is deformed by stretching (structure **2**), the positions of the lower unoccupied and upper occupied states ascend, the position of the latter changing more substantially. The energy gap between the upper occupied and lower unoccupied states (HOMO–LUMO gap) for any of the nanoclusters in question is larger than the band gap of a bulk crystal, which is qualitatively true [1-3, 14]. The shift of the lower unoccupied state obtained in the calculation corresponds to a change in the position of the conduction band bottom in a bulk crystal [14].

Thus, a remarkable variation of the calculated structural properties of strained silicon structures, when interactions with the substrate are taken into account, indicate that in the calculations of parameters of semiconductor nanostructures on substrates not only the geometry should be optimized, but also the conditions on the interface must be considered.

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